

Lateral inhomogeneities in ultrathin metal organic films

R. Fink¹, U. Groh¹, G. Meigs², and H. Ade³

¹Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

²Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

³Dept. of Physics, North Carolina State Univ., Raleigh, NC 27695-8202, USA

INTRODUCTION

There is a rapidly growing interest inorganic thin films since Batlogg et al. have shown that high charge carrier mobilities can be obtained in organic single crystals [1]. With respect to possible applications and handling, thin film growth of organic compounds is advantageous in particular if comparable structural qualities can be achieved. Organic molecular beam epitaxy under ultra-high vacuum conditions has proven to be a suitable technique in particular when using single crystal metal substrates. In many cases the covalent bonding of the molecules to the metal substrate induces long-range ordered domains, which are mainly limited by the size of the substrate terrace [2]. Superstructures are formed which in most cases are commensurate to the substrate lattice. In contrast, on inert substrates molecular self-arrangement is governed by the intermolecular forces thus resulting in polycrystalline films.

Within our current activities we investigated the film growth of metal-organic substances, preferentially so-called charge-transfer (CT) complexes on the basis of TCNQ or DMe-DCNQI molecules. In particular the DCNQI-based materials are promising candidates in molecular electronics since these materials undergo a Peierls transition leading to strong variations in their electric transport properties. For example in deuterated $\text{Cu}(\text{DMe-DCNQI})_2$ single crystals (diameter: several μm) the electric conductivity drops by 8–10 orders in magnitude from a Cu-like behavior to an insulating state upon cooling below 60 K (T_c depends on the degree of deuteration) [3]. Note that so far no long-range ordered films have been prepared from these materials which reflect the physical properties of single crystals.

SAMPLE PREPARATION

In order to or the present investigations we concentrated on TCNQ-based CT complexes using Cu as metallic counter ion. Since our previous experiments on catalytically triggered reactions in sandwich structures showed traces of the chemical reactants we utilized a co-evaporation technique with over-stoichiometric ratio of TCNQ. Conventional Si_3N_4 membranes were utilized as substrates to meet the requirements of scanning transmission x-ray microspectroscopy (STXM). The substrates were kept at room temperature during film deposition and the nominal film thickness was chosen to about 120 nm. Microspectroscopy experiments based on the NEXAFS contrast were carried out at BL 7.0.1-STXM at the Advanced Light Source with a spatial resolution of about 80 nm.

RESULTS

Fig. 1 shows two images recorded at photon energies of 285.0 eV and 289.0 eV, the latter corresponds to the main π^* -absorption resonance of $\text{Cu}(\text{TCNQ})_2$. The scanned area corresponds to $30 \times 30 \mu\text{m}^2$. The contrast in Fig. 1a is due to micro-crystallites of $\text{Cu}(\text{TCNQ})_2$ which form in an average size of $4 \times 10 \mu\text{m}^2$. In between the crystallites, a thinner film of unreacted TCNQ is pres-

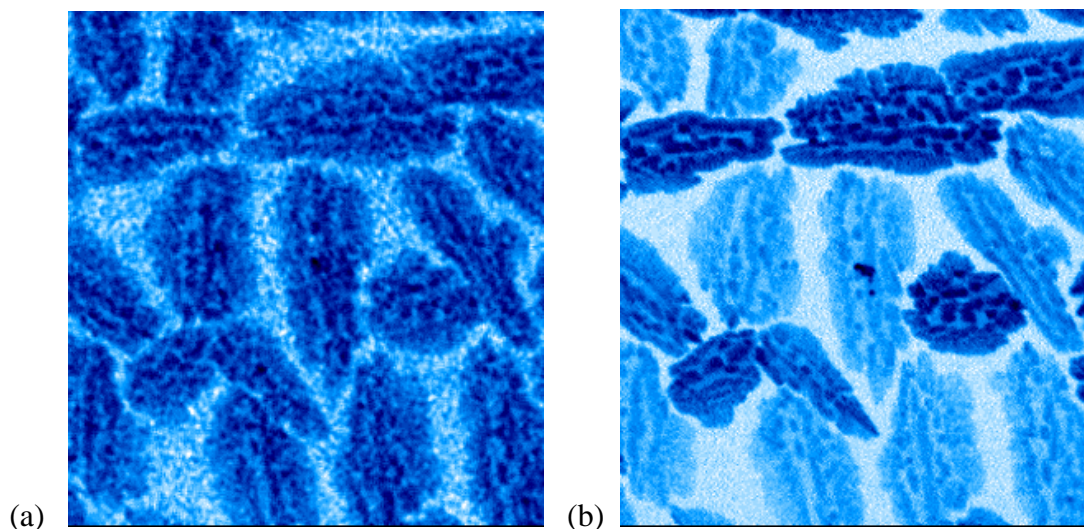


Figure 1. STXM images for co-evaporated $\text{Cu}(\text{TCNQ})_2$ films prepared on Si_3N_4 membranes for two different photon energies, $h\nu = 285$ eV (a) and $h\nu = 289$ eV (b). Nominal film thickness: 120 nm. The scanned area is $30 \times 30 \mu\text{m}^2$ - the polarization vector of the synchrotron radiation is parallel to the x-axis.

ent as derived from local NEXAFS spectra. Very strong differences in the contrast of single crystallites are observed for $h\nu = 289$ eV which corresponds to the first π^* -resonance of $\text{Cu}(\text{TCNQ})_2$. The contrast is due to the linear NEXAFS dichroism and thus allows to deduce the molecular orientation in the crystallites. From the differences for crystallites with their long axis either parallel or perpendicular to the polarization of the synchrotron radiation, we unambiguously may conclude that the molecular plane of the TCNQ molecules is oriented perpendicular to the long axis of the crystallites thus corresponding to the crystalline c-axis. From the ratio between length and width of the crystals we may also conclude that the c-axis reflects the growth direction of the crystallites.

The present data clearly demonstrate that inert substrates like Si_3N_4 are no ideal candidates for organic film growth since the intermolecular forces with preferential structural parameters. With respect to applications metal-organic films with a perpendicular orientation of the crystalline c-axis are preferred. As is known from NEXAFS experiments for TCNQ based CT films on metal single crystals (e.g. $\text{Ag}(111)$) grow in a layer-by-layer mode with a molecular orientation parallel to the substrate. Future STXM experiments will therefore focus on CT films grown on ultrathin metal films to study the lateral homogeneity for different preparation parameters (e.g., substrate temperature, sublimation rate).

REFERENCES

1. J.H. Schön et al. *Science* **29**, 599 (2000); J.H. Schön et al., *Nature* **406**, 702 (2000).
2. D. Gómez, H. Schmitt, J.U. von Schütz, H. Wachtel, and H.C. Wolf, *J. Chem. Phys.* **104**(11), 4198 (1996); D. Bauer et al., *Synthetic Metals* **71**, 1887 (1995).
3. E. Umbach, M. Sokolowski, and R. Fink, *Appl. Physics A* **63**, 565 (1996).

This work was supported by the Bundesminister für Bildung und Forschung, contract 05 SL8 WW1 8. Intense discussions with E. Umbach on the NEXAFS data are gratefully acknowledged.

Principal investigator: Rainer Fink. Experimentelle Physik II, Universität Würzburg.
Email: raifi@physik.uni-wuerzburg.de Telephone: +49-931-888-5163.